

lation of 1.300 electrons for the orbital pair. For the WC surface, a total of 1.184 electrons are transferred, providing 0.592 electrons for each orbital. The occupation of the $2\pi^*$ level and the calculated overlap populations reflect the reduced donor ability of the WC surface. For CO on W(100), the overlap population for the C–O bond is 0.985, while for the WC surface, this value is 1.028, which can be compared with that of free CO which shows an overlap population of 1.32. The W–C overlap populations are 0.999 and 0.928 for the pristine and carbided surfaces, respectively. For the atop sites, the WC surface seems slightly less active, though the values of the overlap populations and $2\pi^*$ occupations suggest similarities between the selected sites consistent with the HREELS studies.

HCN on W(100) and the related carburized surface desorbs molecularly and dissociates into H_2 and N_2 , leaving carbon at the surface. On the carbided surface, a protonation occurs at the nitrogen of the HCN. The decomposition occurs more readily on the pristine surface.¹² The adsorption sites considered for these two surfaces are representative sites selected from studies based on diatomic systems and organometallic models. In both cases, the HCN is assumed to be bent such that the $\angle HCN$ is 120° . The fragment orbital occupations and overlap populations for HCN on these two surfaces are shown in Table II.

The chemistry of the carburized surface is similar to that of the pristine surface; however, the surface structure is sig-

nificantly different to allow for differential adsorption chemistry. The activity of the carbided surface is the result of both bulk carbide interaction and the structural changes induced upon carburization.

¹D. O. Goodman, R. D. Kelley, T. E. Madey, and J. T. Yates, *J. Catal.* **63**, 226 (1980).

²J. A. Rabo, A. P. Risch, and M. C. Poutsma, *J. Catal.* **53**, 295 (1976).

³L. S. Caputi, G. Chairello, and L. Papagno, *Surf. Sci. Lett.* **162**, 259 (1985).

⁴G. Paolucci, R. Rosei, K. C. Prince, and A. M. Bradshaw, *Appl. Surf. Sci.* **22/23**, 582 (1985).

⁵E. I. Ko and R. Madix, *J. Phys. Chem.* **82**, 4019 (1981).

⁶K. A. Pearlstine and C. M. Friend, *J. Am. Chem. Soc.* **107**, 5989 (1985).

⁷See, for example, L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic, New York, 1971); P. Swarzkopf, R. Kieffer, W. Leszynski, and F. Benesovsky, *Refractory Hard Metals* (MacMillan, New York, 1953).

⁸(a) A. L. Hagstrom and L. I. Johansson, *J. Electron Spectrosc. Relat. Phenom.* **11**, 75 (1977); (b) J. Redinger and J. B. Pendry, *Surf. Sci.* **169**, 19 (1985); (c) I. Kojima, M. Orita, and E. Miyazaki, *ibid.* **160**, 153 (1985); (d) C. Oshima, M. Aona, S. Otami, and Y. Ishizawa, *Solid State Commun.* **54**, 827 (1985).

⁹J. B. Benzinger, E. I. Ko, and R. J. Madix, *J. Catal.* **54**, 414 (1974).

¹⁰D. E. Eastman, *Solid State Commun.* **10**, 933 (1972).

¹¹S. S. Sung and R. Hoffmann, *J. Am. Chem. Soc.* **107**, 578 (1985).

¹²C. Oshima, M. Aona, T. Tanaka, S. Kawai, S. Zaima, and Y. Shibata, *Surf. Sci.* **102**, 312 (1981).

¹³S. M. Gates, J. N. Russell, Jr., and J. T. Yates, *Surf. Sci.* **146**, 199 (1984).

¹⁴Personal communication and collaboration with Professor C. M. Friend at Harvard University Chemistry Department.

Summary Abstract: The oxidation of carbon monoxide on the Pt(110)-(1×2) surface: The influence of the adlayer composition on the reaction dynamics

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The study of chemical reaction dynamics on solid surfaces is of fundamental scientific and technological importance. The oxidation of CO on platinum surfaces has attracted particular attention¹ since the reaction probability is high and the product CO_2 molecule interacts "weakly" with the surface upon formation. Consequently, the distribution of energy in the translational and internal modes of the gas phase CO_2 contains information concerning the potential energy surface that describes the elementary bimolecular surface reaction between the adsorbed reactants. A proper interpretation of this detailed dynamical information is aided tremendously by independent knowledge of the integral kinetic rate parameters, i.e., the activation energy and the preexponential factor. In particular, knowledge of the exoer-

gicity of the surface reaction and/or the relative (potential) energy level of the transition state are crucial to a more complete understanding of the surface reaction dynamics.

We have developed and employed the technique of surface temperature modulation to examine the dynamics of the oxidation of CO on the Pt(110)-(1×2) surface.² This technique permits a straightforward analysis of the energetics of elementary surface reactions even in the presence of strong nonlinearities, providing a decided advantage over competing techniques such as modulated molecular-beam reactive scattering. We shall emphasize here the coverage dependence of the kinetic rate parameters (E_a and $k_p^{(2)}$) that describe the elementary surface reaction $CO(a) + O(a) \rightarrow CO_2(g)$. These data will be compared briefly with results

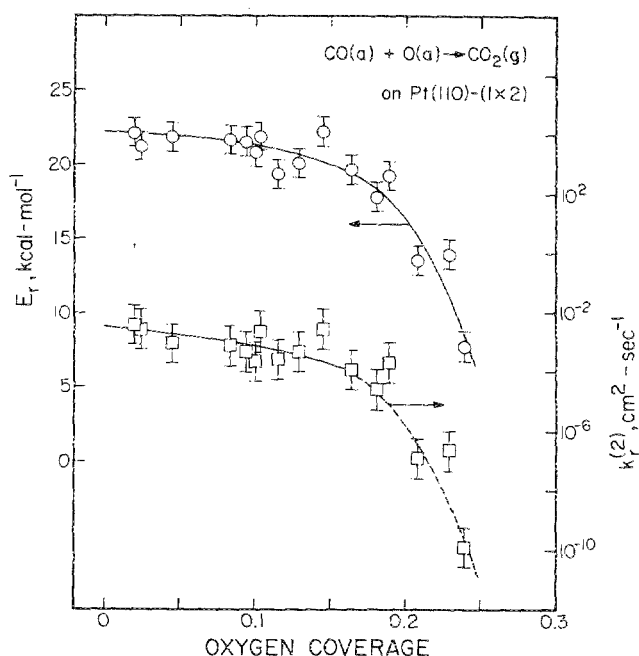


FIG. 1. Activation energy (E_a) and second-order preexponential factor ($k_p^{(2)}$) for the reaction $\text{CO(a)} + \text{O(a)} \rightarrow \text{CO}_2\text{(g)}$ on the $\text{Pt(110)-(1}\times\text{2)}$ surface as a function of the calculated coverage of oxygen adatoms θ_{O} , where $\theta_{\text{O}} = 0.4$ is saturation.

obtained previously concerning the coverage dependence of the energy retained in the translational³ and internal^{4,5} modes of the product CO_2 molecule.

The activation barrier for the elementary bimolecular surface reaction has been evaluated at a variety of steady-state conditions, as described elsewhere.² The observed activation energy has been found to range between approximately 22 and 8 kcal mol^{-1} . Making use of our reaction rate measurements and previously measured rates of adsorption and desorption, the adsorbate concentrations have been calculated for these reaction conditions.⁶ These calculations show that the coverages of both adsorbed reactants vary considerably for the conditions studied (e.g., $0.003 < \theta_{\text{CO}} < 0.27$ and $0.02 < \theta_{\text{O}} < 0.25$). As may be seen in Fig. 1, the magnitude of the activation barrier correlates well with the coverage of oxygen adatoms. In the low coverage limit, the activation energy is $22 \pm 1 \text{ kcal mol}^{-1}$, in excellent agreement with previous results on other platinum surfaces at similar adsorbate concentrations.^{7,8} However, as the fractional coverage of oxygen adatoms increases above approximately 0.15, a precipitous drop in the magnitude of the activation barrier is observed, the variation in the magnitude of the activation energy with oxygen coverage being quite nonlinear. This result can be interpreted qualitatively as a manifestation of the crucial role that the *local* configuration of the reactants plays in determining the surface reaction dynamics. At relatively high oxygen coverages ($\theta_{\text{O}} > 0.15$) adsorbed CO reacts in regions of high local oxygen adatom concentration. In these regions of the surface, the adsorbed reactants have reduced binding energies, which leads directly to a decrease in the activation energy for the production of CO_2 .

The preexponential factor for the elementary bimolecular

surface reaction has been evaluated also for these reaction conditions. Measurement of the apparent rate coefficient (which is related simply to the true rate coefficient⁶) and utilizing both the calculated adsorbate concentrations and the independently measured activation energy permits the calculation of the corresponding values for the second-order preexponential factor. These values of the preexponential factor are displayed in Fig. 1 as a function of the oxygen adatom concentration. As with the activation energy, the magnitude of the preexponential factor correlates well with the coverage of oxygen adatoms. In the limit of low coverages, the preexponential factor approaches a value of approximately $3 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, in reasonable agreement with a previous result obtained on Pt(111) ($10^{-1} \text{ cm}^2 \text{ s}^{-1}$)⁷ and in excellent agreement with the "normal" value of 10^{-2} – $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ predicted by transition state theory. As the oxygen concentration increases beyond $\theta_{\text{O}} \approx 0.15$, the magnitude of the preexponential factor drops precipitously in concert with the activation energy. For example, as the activation energy drops continuously to values from approximately 13 to 8 kcal mol^{-1} , the preexponential decreases to values from approximately 10^{-7} to $10^{-10} \text{ cm}^2 \text{ s}^{-1}$. These former values are in excellent agreement with previous results at similar high oxygen adatom coverages on other platinum surfaces, e.g., on Pt(111) ($E_a \approx 11$ – 12 kcal mol^{-1} and $k_p^{(2)} \approx 2 \times 10^{-7}$ – $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)⁷ and on a stepped $\text{Pt}[9(111) \times (100)]$ surface ($E_a \approx 10 \text{ kcal mol}^{-1}$ and $k_p^{(2)} \approx 10^{-7} \text{ cm}^2 \text{ s}^{-1}$).⁹ The major factor contributing to the marked decrease in the preexponential factor is probably associated with local interactions between the adsorbed reactants (as with the activation energy) and not with the formation of separate adsorbate domains. In particular, it is possible that the configuration of reactants which leads to the observed decrease in the activation energy occurs with a very low probability (i.e., on the order of 10^{-7}).⁶ This, then, could explain the anomalously low preexponential factors observed at high oxygen adatom coverages.

These results, especially those concerning the variation of the activation energy with oxygen coverage, are particularly interesting in view of recent investigations studying the distribution of energy in the translational³ and internal modes^{4,5} of the product CO_2 molecule. On a Pt(111) surface, Segner *et al.*³ have observed an increase in the (average) amount of excess translational energy (inferred from the angular distribution of the "desorbing" product CO_2) retained by the product CO_2 molecule with increasing oxygen coverage. Since the angular distribution could always be described by a bimodal distribution (one $\cos \theta$, channel and one $\cos^2 \theta$, channel), this result was interpreted in terms of the degree of thermal accommodation of the product molecule by the surface. It was proposed that step and defect sites provided a significant fraction of the reaction sites at low oxygen coverages, the defect sites being presumably more efficient in energy transfer with the product molecule in comparison to (111) terrace sites. Thus at low oxygen coverages, energy transfer between the product molecule and the surface is more efficient, and the product molecule retains less excess translational energy. This viewpoint downplays any effects due to the increasing exoergicity of the surface